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(54) Title: METHOD FOR PRODUCING HYDROCARBONS

(57) Abstract

This invention relates to a method for producing hydrocarbons with the simultaneous preparation of hydrogen in the reaction with iodine. Aliphatic saturated hydrocarbons, especially methane or ethane, are reacted with iodine, this reaction being conducted preferably in the presence of a catalyst, preferably at a temperature of 400–1200 °C, with the iodine/hydrocarbon molar ratio of 0,1 to 4,0, preferably with bromine addition, preferably by activation using a method of electric discharges and/or activation employing a method of electromagnetic radiation. After the reaction of hydrocarbons with iodine, hydrogen iodide and unreacted iodine are isolated from the mixture of hydrocarbons, said hydrogen iodide is decomposed into iodine and hydrogen, said iodine being recycled to the process, if need be, or hydrogen and hydrocarbons are separated and the reaction residue can be recycled to the process. In an optional solution, unsaturated hydrocarbons having a lower atomic ratio of carbon to hydrogen are used thus obtaining hydrocarbons of a larger carbon/hydrogen atomic ratio.

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METHOD FOR PRODUCING HYDROCARBONS

This invention relates to a method of producing hydrocarbons with the simultaneous preparation of hydrogen.

A method is known for producing hydrocarbons with simultaneous preparing hydrogen by means of a high-temperature pyrolysis, an electric-arc pyrolysis and a catalytic hydrogenation of hydrocarbons. A synthesis from methanol or chemical gas is also known.

A method referred to in U.S. Patent Specification No. 3 119 881 consists in that hydrocarbons are iodinated with iodine and then its reclaiming by means of metallic copper.

Another known method described in U.S. patent specification No. 3 106 590 consists in iodination of hydrocarbons with metal iodides and coincident oxidation of hydrogen iodide with oxygen.

The known iodination processes are complicated technologically because of difficult procedures of separating hydrocarbons from iodine and hydrogen iodide, and the aggressive medium of reaction.

The method for producing hydrocarbons according to the present invention consists in that said hydrocarbons are reacted with iodine in a molar ratio iodine/hydrocarbons of 0,1 to 4,0, preferably with a bromine addition. Aliphatic saturated hydrocarbons are reacted with said iodine to obtain aliphatic saturated and/or unsaturated hydrocarbons. In an optional solution, unsaturated hydrocarbons of lower atomic ratio carbon to hydrogen are used thus hydrocarbons having a larger carbon/hydrogen atomic ratio are obtained.

After the reaction, hydrogen iodide and unreacted iodine are separated from the hydrocarbon mixture, said hydrogen iodide is decomposed into iodine and hydrogen, and said iodine being recycled, if necessary, to the process, or hydrogen and hydrocarbons are separated after the reaction of hydrocarbons with iodine, whilst the reaction residue being recycled, if need be, to the process.

It is advantageous to conduct the reaction of hydrocarbons and iodine by activation using a method of electric discharges and/or activation with an

electromagnetic radiation method.

The reaction of hydrocarbons with iodine and the hydrogen iodide decomposition can also be effected advantageously in a membrane reactor. In a membrane separator, unreacted iodine and hydrogen iodide are separated from hydrocarbon mixture, as well as hydrogen from hydrocarbons.

In both methods it is useful to employ a catalyst supported by rhodium, palladium, platinum or nickel.

The advantage of the method for producing hydrocarbons according to the invention is a possibility for simultaneously obtaining the hydrocarbons and hydrogen in a relatively simple and low energy-consuming process. Moreover, in the method according to the invention the reaction medium is not too aggressive.

Example I. The reaction is conducted at atmospheric pressure and a temperature of 750°C with respect to the mixture having an iodine/methane molar ratio of 3:1 using the nickel catalyst. The obtained methane conversion is 49% and selectivity to ethylene about 75%. After cooling to an ambient temperature, iodine and hydrogen iodide are isolated from the reaction products and a mixture of hydrocarbons comprising methane, ethylene, acetylene and other hydrocarbons is obtained. Iodine and hydrogen iodide are separated by distillation from a washing system, said hydrogen iodide is decomposed into iodine and hydrogen at a temperature of 950°C, whereupon said hydrogen is liberated after cooling in the separator.

Example II. The reaction is carried out as in Example I at a temperature of 850°C. The products obtained are separated without cooling in said membrane separator into a mixture containing hydrogen/hydrocarbons and iodine/hydrogen iodide. The stream of iodine and hydrogen iodide is recycled to the process whilst the reaction of decomposing said hydrogen iodide is conducted on nickel catalyst at a temperature of 950°C. Hydrogen is isolated in said membrane separator and the obtained iodine is recycled into the reaction whilst mixing with methane.

Example III. Procedure is the same as in Example I, and iodination reaction is conduced in the membrane reactor. Then proceeding is performed as in Example II. The obtained methane conversion amounts to about 67% and selectivity to ethylene approximately 75%.

Example IV. The reaction is carried out at atmospheric pressure and a temperature of 900°C for the mixture having a iodine/ethylene molar ratio of 2: 1 on the nickel catalyst. The obtained products are separated without cooling in said membrane separator to yield a mixture containing hydrogen and hydrocarbons, iodine and hydrogen iodide. The stream of iodine and hydrogen iodide is recycled to the process whilst the reaction of decomposing said hydrogen iodide is conducted on nickel catalyst at a temperature of 950°C. Hydrogen is isolated in said membrane separator and the obtained iodine is recycled into the reaction whilst mixing with methane. The obtained ethylene conversion is 89% and selectivity to acetylene about 65%.

WE CLAIM

1. A method for producing hydrocarbons with the simultaneous preparation of hydrogen while reacting with iodine, preferably in the presence of a catalyst, and preferably at a temperature of 400-1200°C, characterised is that aliphatic saturated hydrocarbons, especially methane or ethane, are subjected to a reaction with iodine, wherein said reaction is conducted in a molar ratio iodine/hydrocarbons of 0,1 :4,0, preferably with bromine addition, whereupon hydrogen iodide and unreacted iodine are isolated from the mixture of hydrocarbons, said hydrogen iodide is decomposed to give iodine and hydrogen, and if need be, said iodine being recycled to the process or, after reacting hydrocarbons with iodine, hydrogen and hydrocarbons are separated, and the reaction residue is, if need be, recycled to the process.
2. A method as claimed in claim 1 wherein said reaction of hydrocarbons with iodine is conducted by activation using a method of electric discharges and/or activation via a method of electromagnetic radiation.
3. A method as claimed in claim 1 wherein supported rhodium, palladium, platinum or nickel are used as a catalyst.
4. A method as set forth in claim 1 wherein said reactions of aliphatic saturated hydrocarbons with iodine and the hydrogen iodide decomposition are conducted in a membrane reactor.
5. A method as claimed in claim 1, characterised in that unreacted iodine and hydrogen iodide are separated from the mixture of hydrocarbons, and hydrogen from hydrocarbons, in a membrane separator.
6. A method for producing hydrocarbons with simultaneously preparing hydrogen by a reaction with iodine, preferably in the presence of a catalyst, and preferably at a temperature of 400-1200°C, characterised in that unsaturated hydrocarbons having a lower carbon/hydrogen atomic ratio are subjected to the reaction with iodine to obtain hydrocarbons of a larger carbon to hydrogen ratio and said reaction being conducted in the molar ratio iodine to hydrocarbons of 0,1:0,4, preferably with

bromine addition, whereupon hydrogen iodide and unreacted iodine are isolated from the mixture of hydrocarbons, said hydrogen iodide is decomposed into iodine and hydrogen and, if need be, said iodine is recycled to the process or, after reaction of hydrocarbons with iodine, said hydrogen and hydrocarbons are separated and the reaction residue is, if need be, recycled to the process.

7. A method as claimed in claim 6 wherein said reaction of hydrocarbons with iodine is conducted by activation using a method of electric discharges and/or activation through a method of electromagnetic radiation.
8. A method as claimed in claim 6 wherein supported rhodium, palladium, platinum or nickel are used as a catalyst.
9. A method as claimed in claim 6 wherein the reaction of aliphatic unsaturated hydrocarbons with iodine and the decomposition of hydrogen iodide are carried out in the membrane reactor.
10. A method of claim 6 wherein unreacted iodine and hydrogen iodide are separated from the mixture of hydrocarbons, as well as hydrogen from hydrocarbons, in the membrane separator.

INTERNATIONAL SEARCH REPORT

Intern ıal Application No
PCT/PL 99/00019

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C5/44

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 793 214 A (NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ) 9 April 1958 (1958-04-09) claims 1,4 ---	1-10
Y	GB 978 181 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 9 May 1963 (1963-05-09) page 1, line 55-64 -page 2, line 35-40 -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 793214 A		NONE	
GB 978181 A		NONE	